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# In-Situ Imaging of Chloride Ions at the Metal/Solution Interface by Scanning Combination Microelectrodes

C.-J. Lin, R.-G. Du,\* and T. Nguyen\*\*

## ABSTRACT

Combination solid silver-silver chloride (Ag-AgCl) and liquid membrane  $\text{Cl}^-$  ion-selective microelectrodes were designed and constructed. These microelectrodes, which had a micrometer-sized tip, contained two compartments: one served as the reference electrode and the other as the  $\text{Cl}^-$  ion-selective electrode. The microelectrodes were used to map in-situ  $\text{Cl}^-$  ion distribution in several localized corrosion systems. When used with a computerized scanning stage, the microelectrodes provided information on the distribution of  $\text{Cl}^-$  ions near the metal/electrolyte interface.  $\text{Cl}^-$  ions were observed migrating toward and accumulating near the anodic region forming a " $\text{Cl}^-$  ion-rich island" on the metal surface. Scanning combination  $\text{Cl}^-$  ion-selective microelectrodes may provide a useful tool for mechanistic studies of localized corrosion.

**KEY WORDS:** chloride ion concentration, imaging, localized corrosion, scanning chloride ion-selective microelectrode

## INTRODUCTION

In the environment,  $\text{Cl}^-$  ions are so influential to various types of localized corrosion such as pitting corrosion, crevice corrosion, and stress corrosion cracking that the study of the role of the  $\text{Cl}^-$  ion in local breakdown of passivity and localized corrosion

of metals has become one of the most critical subjects in corrosion science. Although a number of theoretical models relating  $\text{Cl}^-$  ion aggression to the breakdown of passivity and initiation of localized corrosion have been proposed,<sup>1-6</sup> experimental evidence of the  $\text{Cl}^-$  ion behavior in microenvironments close to the metal/solution interface is still scarce.

Techniques based on microelectrodes have been developed and applied to measure the  $\text{Cl}^-$  ion concentration in occluded areas of localized corrosion.<sup>7-9</sup> However, for many localized corrosion systems, inserting a single  $\text{Cl}^-$  ion microelectrode into the localized corrosion area or scanning it over a local corroded surface may cause serious error in the measurement of  $\text{Cl}^-$  ion concentration. This is a result of the effects of corrosion potential on the  $\text{Cl}^-$  ion concentration in the occluded area. The measured potential of a  $\text{Cl}^-$  electrode ( $E_{\text{meas}}$ ) is the sum of the potential of  $\text{Cl}^-$  ion in the solution ( $E_{\text{Cl}^-}$ ) and the potential caused by the corrosion reaction ( $E_{\text{corr}}$ ):

$$E_{\text{meas}} = E_{\text{Cl}^-} + E_{\text{corr}} \quad (1)$$

For localized corrosion,  $E_{\text{corr}}$  may be different at different microsites.  $E_{\text{corr}}$ -measured values can be compensated by a reference electrode only if the  $\text{Cl}^-$  probe and the tip of the reference electrode are placed at approximately the same location. Further, it is often difficult to measure accurately  $\text{Cl}^-$  ion concentration in a microarea if the tip of the probe is not small enough and the reference electrode is far away from the  $\text{Cl}^-$  ion sensitive probe.

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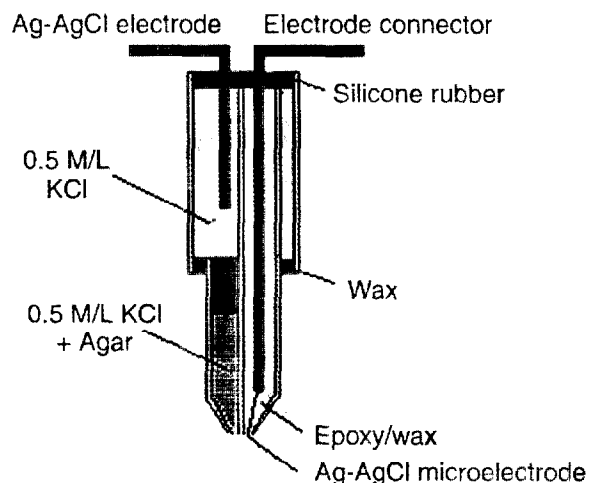


FIGURE 1. Combination solid Ag-AgCl Cl<sup>-</sup> ion-selective microelectrode.

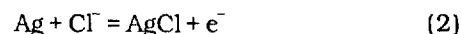
Ex-situ measurements of two-dimensional Cl<sup>-</sup> ion distribution on a metal surface by using surface analytical techniques such as Auger electron spectroscopy, x-ray photoelectron spectroscopy, etc., can be performed only in a high vacuum, which requires the corrosion process stopped. Obviously, these methods cannot provide direct and dynamic information on Cl<sup>-</sup> behavior at the metal/solution interface.<sup>10-11</sup> Thus, it is important to develop microprobes to map in-situ distribution of Cl<sup>-</sup> ions at the metal/electrolyte interface. This information is essential for a better understanding of the role of Cl<sup>-</sup> ions in the localized corrosion of metals.

The present study described preparation and presented experimental results to demonstrate the application of two types of combination Cl<sup>-</sup> ion-selective microelectrodes: one based on a solid silver-silver chloride (Ag-AgCl) electrode and the other based on a liquid membrane. Using these two types of combination microelectrodes with a computerized scanning stage, two-dimensional distributions of Cl<sup>-</sup> ions close to a metal/solution interface was imaged for the first time for different types of localized corrosion. The role of Cl<sup>-</sup> ion preferential adsorption and accumulation on a metal surface on the initiation and propagation of localized corrosion was presented and discussed.

## EXPERIMENTAL PROCEDURES

### Combination Solid Ag-AgCl Cl<sup>-</sup> Ion — Selective Microelectrode

The Ag-AgCl electrode is, by far, the most frequently used reference electrode and Cl<sup>-</sup> ion sensor electrode because it is simple to prepare, reliable, and reproducible. The half-cell reaction of an Ag-AgCl system and its corresponding potential are the following:



$$E_{\text{Cl}^-} = E_{\text{ref}} + 2.303 RT / F \log a_{\text{Cl}^-} \quad (3)$$

where  $E_{\text{ref}}$  is the reference potential,  $R$  is the gas constant (8.314 JK<sup>-1</sup>/mol),  $T$  is the absolute temperature (K),  $F$  is Faraday's constant (96,485 C/mol), and  $a_{\text{Cl}^-}$  is the Cl<sup>-</sup> ion activity. Equation (2) explicitly illustrates that the potential of an Ag-AgCl system is dependent on the Cl<sup>-</sup> ion concentration in the sample.

Figure 1 illustrates a schematic arrangement of a combination solid Ag-AgCl Cl<sup>-</sup> ion-selective microelectrode. It consisted of two compartments: one served as the reference electrode and the other acted as the Cl<sup>-</sup> ion-selective electrode. It was prepared by pulling, under electrical heating, a heavy-walled, double-barreled, 1.5/0.8-mm (outer diameter [OD]/inner diameter [ID]) borosilicate glass capillary into a point-shaped micropipette. The tip of the barrel used for containing the Cl<sup>-</sup> ion-selective electrode was truncated. The other barrel was filled with an agar gel containing a 0.5-M/L potassium chloride (KCl) solution, which served as the Luggin bridge of the Ag-AgCl reference electrode. The construction of the Cl<sup>-</sup> ion-selective microelectrode has been described in detail previously.<sup>7</sup> Briefly, it was made of a 0.1-mm diameter, high purity (99.9%) silver wire. After sharpening one end to produce a tip diameter of ~ 10 μm, the silver wire was electrodeposited with AgCl. Except for the uncoated tip, the AgCl-deposited Ag (hereafter called Ag-AgCl) wire was coated with an epoxy material. The Ag-AgCl wire with a tip of ~ 10 μm diameter was inserted into the truncated barrel and secured with paraffin wax at both ends. The barrel containing the Ag-AgCl wire served as the Cl<sup>-</sup> ion-selective microelectrode. The micro Luggin bridge was connected to a glass tube (ID: 3 mm) and sealed with molten wax at the joint. The glass tube then was filled with 0.5 M/L KCl electrolyte, which served as an internal reference solution. Finally, a regular 250-μm diameter Ag-AgCl electrode was placed in the glass tube, and the top ends of the reference electrode and Cl<sup>-</sup> ion-selective electrode compartments were sealed with a silicone adhesive.

### Combination Liquid Membrane Cl<sup>-</sup> Ion — Selective Microelectrode

Liquid membrane ion-selective electrodes have been well developed and applied in biological and medical sciences.<sup>12-14</sup> The potential across a liquid membrane is composed of a diffusion potential within the membrane and an equilibrium potential at the phase boundary. Ideally, this potential difference should be a linear function of the logarithm of the activity of the ion. If all other potential differences are assumed to be constant, the measured potential for a

liquid membrane electrode is described by the Nernst equation:

$$E_{\text{Cl}^-} = E_{\text{ref}} + 2.303 RT / F \log a_{\text{Cl}^-} \quad (4)$$

Combination liquid membrane  $\text{Cl}^-$  ion-selective microelectrodes were designed and constructed in this study for in-situ imaging  $\text{Cl}^-$  ion concentration in localized corrosion systems. Similar to the solid Ag-AgCl-based probe, the combination liquid membrane  $\text{Cl}^-$  microelectrode contained two compartments: one served as the reference electrode and the other was the  $\text{Cl}^-$  ion-sensitive electrode (Figure 2). The combination liquid membrane  $\text{Cl}^-$  ion-selective microelectrodes were prepared by pulling a clean, double-barreled, 1.5/0.8-mm (OD/ID) borosilicate glass tube into a point-shaped micropipette, which contained two capillaries, each had an ID of  $\approx 1 \mu\text{m}$ . The capillaries were exposed to a 5% mass fraction of dimethyldichlorosilane solution in xylene for  $\approx 2$  min, followed by heating at  $100^\circ\text{C}$  for 1 h. This process was necessary to improve the adhesion between the membrane liquid (ion-selective exchanger) and the capillary glass surface. After silanization, one of the capillaries was filled with a  $\text{Cl}^-$  ion-selective exchanger and the other was filled with an agar gel containing 0.5 M/L KCl solution. The length of the ion exchanger in the microcapillaries was  $\sim 200 \mu\text{m}$  from the tip. After filling both capillaries with 0.5 M/L KCl, which served as an internal solution for the ion-selective electrode and the reference electrode, Ag-AgCl wires then were inserted into the two separate capillaries. Wax and silicone adhesive were used to seal the joints, capillary ends, and the solid Ag/AgCl microelectrode. All steps involved in the preparation of the combination solid and liquid membrane  $\text{Cl}^-$  ion-selective microelectrodes were carried out under a light microscope. The body of the liquid membrane,  $\text{Cl}^-$  ion-selective microelectrode, was attached to a glass tube having a diameter of 4 mm and a height of 30 mm to facilitate handling.

### Scanning with $\text{Cl}^-$ Microelectrodes

The scanning reference electrode technique (SRET) has been used for studying the potential distribution of localized corrosion.<sup>15</sup> An improved computerized system for scanning ion-selective microelectrodes has been developed recently for imaging  $\text{Cl}^-$  ion concentration in localized corrosion studies.<sup>16-17</sup> For this new scanning stage, a preamplifier with high-input impedance was added to the system to permit the imaging of  $\text{Cl}^-$  ion concentration close to the metal/solution interface. This modification was necessary because the internal impedance of a liquid membrane  $\text{Cl}^-$  ion-selective microelectrode is higher than that of a reference microelectrode. Figure 3 illustrates the scanning system used for imaging  $\text{Cl}^-$  ions by  $\text{Cl}^-$  ion-selective microelectrodes.

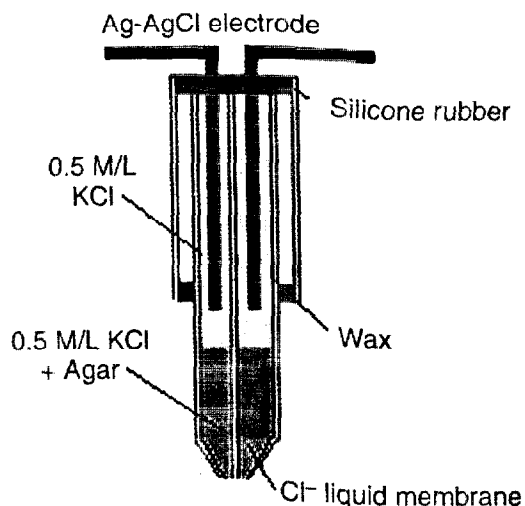


FIGURE 2. Combination liquid membrane  $\text{Cl}^-$  ion-sensitive microelectrode.

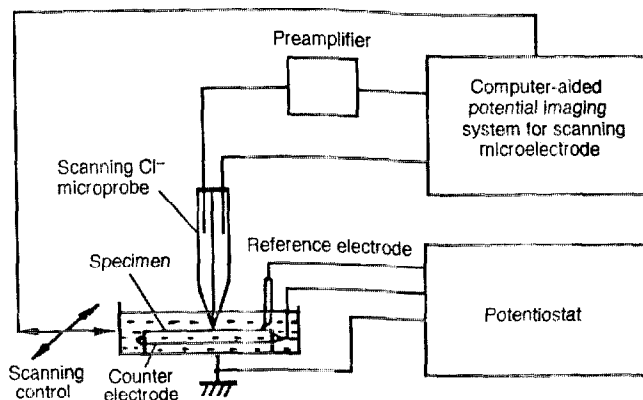


FIGURE 3. A schematic of the scanning system for use with the microelectrodes to measure  $\text{Cl}^-$  ion concentration near the electrolyte/metal interface.

### Measurement Procedures

Two main experiments were carried out. One was used to assess the feasibility and sensitivity of the two  $\text{Cl}^-$  microelectrodes developed for imaging in-situ  $\text{Cl}^-$  ions near a metal/electrolyte interface; the other was to apply these microelectrodes for following the distribution of  $\text{Cl}^-$  ions in localized corrosion.

For the first experiment, a simulated microgalvanic arrangement consisting of an anode and a cathode having different surface areas was constructed to simulate a localized corrosion system (Figure 4). To prepare the specimens for this investigation, a hole having a diameter of 1 mm and a length of 10 mm was drilled into the center of a copper cylinder, which had a dimension of 8 mm in diameter and 10 mm in length. After inserting an 80- $\mu\text{m}$  diameter Pt wire into the hole and insulating

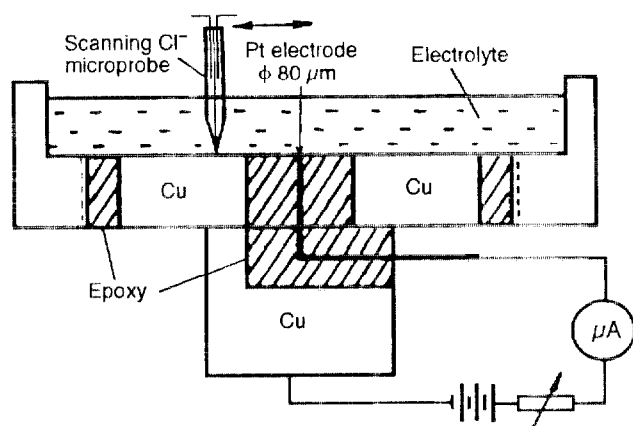


FIGURE 4. A simulated galvanic system having different anode and cathode surface areas used to test the feasibility of measuring  $\text{Cl}^-$  ion distribution in localized corrosion by microelectrodes.

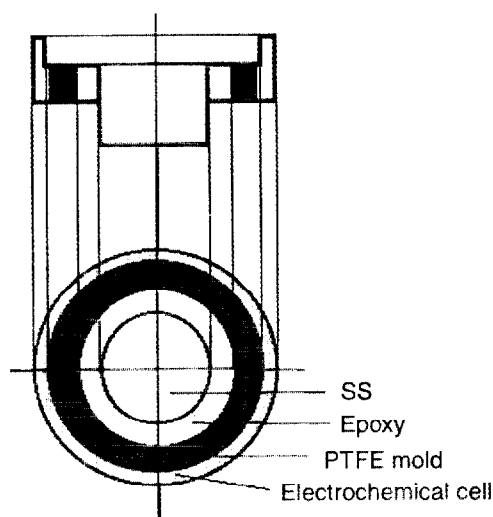


FIGURE 5. Configuration of a SS specimen used for measuring  $\text{Cl}^-$  ion distribution in crevice and pitting corrosion.

the Pt wire from the copper wall with an epoxy, the surface of the copper cylinder with the imbedded Pt wire was polished. The copper cylinder was mounted onto a plastic mold 20 mm in diameter, with epoxy material, as a regular sample preparation for the electrochemical test. The Pt wire and copper cylinder were connected through a battery to an adjustable resistance and a microammeter. A plastic cylinder, which served as the liquid cell to contain the test electrolyte, having a diameter of 30 mm and a height of 10 mm, was connected to the sample copper cylinder by a screw. After positioning the  $\text{Cl}^-$  ion-selective microelectrode and then filling the cell with 20 mL of a 0.02-M/L dipotassium phosphate ( $\text{K}_2\text{HPO}_4$ ) solution, the polarity and activity of the simulated

galvanic system were measured. The  $\text{Cl}^-$  ion concentration distributions on the surface of simulated galvanic electrode were recorded for different experimental conditions.

Experiments used to test the applicability of  $\text{Cl}^-$  microelectrodes for studies of localized corrosion were carried out using commercial 18/8 stainless steel (type 304 SS [UNS S30400]<sup>(1)</sup>). This material contained 18.40% Cr, 9.55% Ni, 0.85% Si, 1.38% Mn, 0.91% C, 0.04% P, 0.010% S, and bal. Fe (all percentages are expressed as mass fraction). Figure 5 presents the specimen configuration for mapping the  $\text{Cl}^-$  ion in localized corrosion areas using  $\text{Cl}^-$  ion-selective microelectrodes. Specimens were prepared by placing a SS cylinder of 6 mm in diameter and 20 mm in height in a cylindrical polytetrafluoroethylene (PTFE) mold; the latter had a diameter twice that of the SS cylinder. An epoxy-molding compound was poured into the mold just slightly below the SS cylinder surface. After the epoxy was cured, the surface of the SS cylinder imbedded in the epoxy was mechanically polished; the last polish was with a 0.5- $\mu\text{m}$  diamond paste. After polishing, the test surface was cleaned with methanol followed by triply distilled water. The epoxy-molded SS specimen with the PTFE mold then was fit into a plastic electrochemical cell, which was held to the PTFE mold with screws. Wax was used to seal the space between the PTFE mold and the plastic electrochemical cell. Platinum wire, which served as the counter electrode, was arranged in circles, concentric with the specimen surface.

In this way, a uniform polarization current was maintained on the specimen surface through the use of a low-noise potentiostat. Each specimen was placed on the scanning stage with the testing surface upward. After carefully adjusting the  $\text{Cl}^-$  ion-selective electrode to  $\sim 5 \mu\text{m}$  from the specimen surface with a light microscope, a test solution was placed into the holder (cell) with a syringe. Three electrolytes: 0.1 M/L sodium chloride ( $\text{NaCl}$ ), 0.5 M/L ferric chloride ( $\text{FeCl}_3$ ), and 0.02 M/L  $\text{K}_2\text{HPO}_4$  were used as test solutions. The depth of the test solution in the cell never exceeded 8 mm. All experiments were carried out in air and at ambient temperature ( $\sim 25^\circ\text{C}$ ).

## RESULTS AND DISCUSSION

### Calibration of the Combination $\text{Cl}^-$ Ion-Selective Microelectrodes

Figure 6 displays the calibration curves for combination solid Ag-AgCl (Curve 1) and combination liquid membrane (Curve 2)  $\text{Cl}^-$  ion-sensitive microelectrodes. The symbols are experimental data and the lines are used to connect the data points in the figure. Results were obtained by measuring the relative potential as a function of  $\text{NaCl}$  concentration in water. A comparison of the calibration curves given in Figure 6 indicates that the two  $\text{Cl}^-$  ion probes pre-

<sup>(1)</sup> UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

pared had similar sensitivity toward  $\text{Cl}^-$  ions. Ag-AgCl  $\text{Cl}^-$  ion-sensitive electrodes are known to give a Nernstian response with  $\text{Cl}^-$  concentration. They may have good stability, fast response, and low resistance. However, it was very difficult to build a combination Ag-AgCl electrode with a micrometer-sized tip diameter. However, it was relatively easy to prepare a combination liquid membrane  $\text{Cl}^-$  ion-selective electrode with a micrometer-sized tip. Liquid membrane ion electrodes usually have high resistance and poor durability. Thus, freshly prepared liquid membrane ion-selective electrodes were used for each experiment.

### Sensitivity of the Combination $\text{Cl}^-$ Ion-Selective Microelectrodes

Figure 7(a) presents mapping of the  $\text{Cl}^-$  ion concentration in the specimen described in Figure 4. Results were recorded by scanning a  $\text{Cl}^-$  ion-selective liquid membrane microelectrode. The measurements started when 0.5 mL of the 1-M/L NaCl solution was added to the cell that had contained 20 mL of the 0.02 M/L  $\text{K}_2\text{HPO}_4$  and when a 61- $\mu\text{A}$  external current was applied to keep the Pt wire as an anode. Figure 7(a) reveals a much higher local  $\text{Cl}^-$  ion concentration in the region near the Pt electrode than in the surrounding area. A stable image of  $\text{Cl}^-$  ion distribution could not be obtained with  $\text{Cl}^-$  ion-selective electrodes if  $\text{Cl}^-$  ions were not present in the solution because a  $\text{Cl}^-$  equilibrium must be established for  $\text{Cl}^-$  ion-selective electrodes. When the Pt electrode was controlled as a cathode and a 122- $\mu\text{A}$  cathodic current was applied to the electrochemical cell, the  $\text{Cl}^-$  ion map results showed no difference in the  $\text{Cl}^-$  ion concentration over the whole scanning area (Figure 7(b)). The same results were observed with a combination solid Ag-AgCl  $\text{Cl}^-$  ion-selective microelectrode.

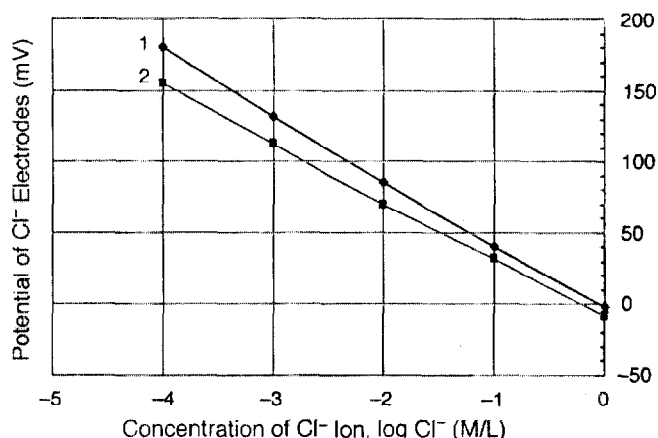


FIGURE 6. Calibration curves for the combination solid Ag-AgCl microelectrode (Curve 1) and the combination liquid membrane  $\text{Cl}^-$  ion-sensitive microelectrode (Curve 2).

Figure 7 results indicated that, under an anodic electrical field,  $\text{Cl}^-$  ions in the solution migrated to and accumulated in the anodic region. Because of the nonuniformity of the electrical field around the scanning area, such movement may result in a nonuniform distribution of  $\text{Cl}^-$  ions at the metal/solution interface. The nonuniform electrical field distribution at the metal/solution interface has been explained by the inhomogeneity of the metal surface.<sup>10-11</sup> These data suggested that  $\text{Cl}^-$  ions may accumulate at anodic defects or inclusion sites where they may induce the initiation of localized corrosion. Under these circumstances, the critical concentration of the aggressive anions is achieved first near those areas of the surface that dissolve at the highest rate. Such nonuniform distribution of the  $\text{Cl}^-$  ion, called " $\text{Cl}^-$  ion-rich island" has been attributed as an important

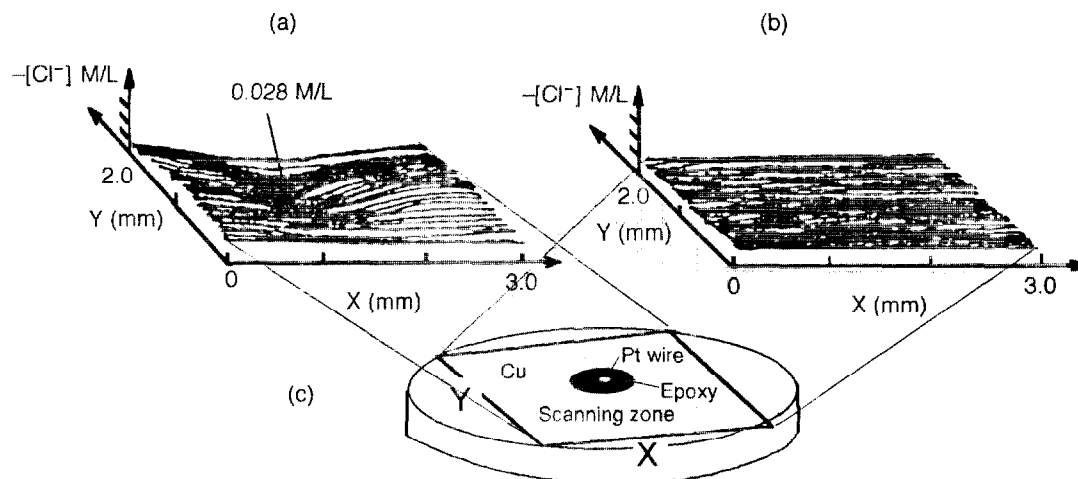
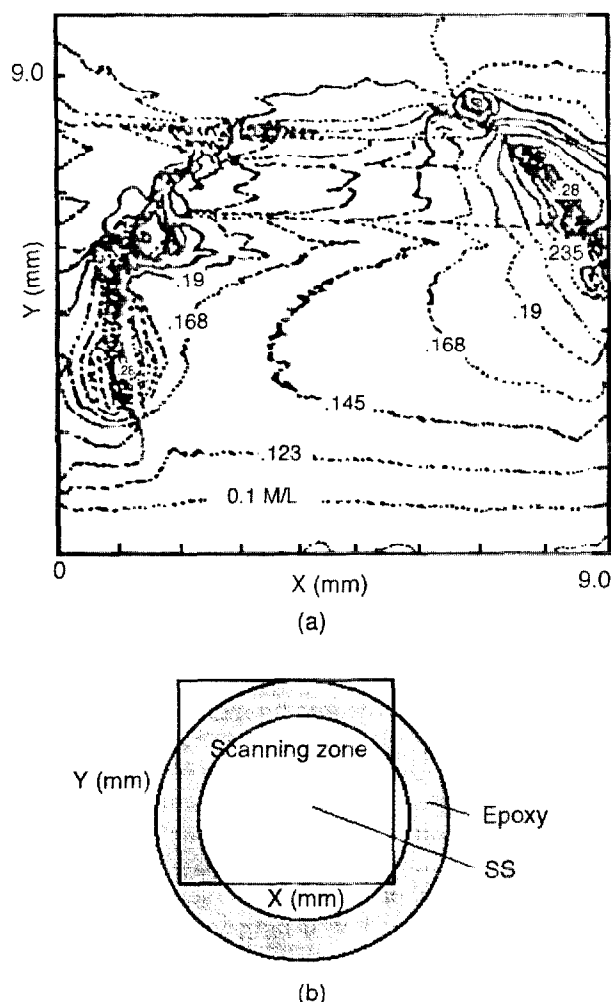


FIGURE 7.  $\text{Cl}^-$  ion concentration distribution for the simulated galvanic system measured by a liquid membrane  $\text{Cl}^-$  microelectrode with: (a) Pt electrode as an anode, (b) Pt electrode as a cathode, and (c) a physical picture of the sample correlated to the  $\text{Cl}^-$  images, in 20 mL 0.02 M/L  $\text{K}_2\text{HPO}_4$  + 0.5 mL 1.0 M/L NaCl solution.



**FIGURE 8.**  $\text{Cl}^-$  ion concentration contour map obtained using solid  $\text{Cl}^-$  ion-selective microelectrode for a 18/8 SS surface in 0.1 M/L NaCl solution when crevice corrosion occurred: (a) a physical picture of the sample correlated to the (b)  $\text{Cl}^-$  image.

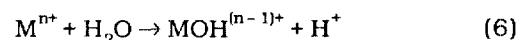
cause of localized corrosion initiation in favorable sites.<sup>17-19</sup>

When the anodic area was much larger than the cathodic area,  $\text{Cl}^-$  ions were not able to accumulate in the anodic region and form a difference in  $\text{Cl}^-$  concentration. In this case, a uniform  $\text{Cl}^-$  ion distribution was observed (Figure 7(b)). Results of Figures 7 demonstrated that effects of different experimental conditions on the distribution of the  $\text{Cl}^-$  ion concentration near the metal/electrolyte interface can be imaged conveniently by scanning  $\text{Cl}^-$  ion-selective microelectrodes.

### Crevice Corrosion

The application of the combination solid Ag-AgCl  $\text{Cl}^-$  ion-selective microelectrode for the studies of crevice corrosion in a chloride environment is demonstrated in Figure 8. These results were obtained using the SS specimen given in Figure 5. In this

case, the SS surface was exposed to a 0.1-M/L NaCl solution and polarized at 0.2  $V_{\text{Ag-AgCl}}$ . The data displayed on the contour lines of Figure 8 indicate the concentration of  $\text{Cl}^-$  ions (in M/L) over the scanned surface (below the mapping image). Figure 8 shows a much higher concentration of  $\text{Cl}^-$  ions along the junction between the SS surface and the epoxy material than in the bulk when crevice corrosion occurred. Further, the  $\text{Cl}^-$  ion concentration at the crevice opening was found to be nearly three times higher than that in the bulk solution. The  $\text{Cl}^-$  ion concentration in an occluded region of a crevice has been reported as high as tenfold than in the bulk.<sup>20</sup> The increase of  $\text{Cl}^-$  ion concentration at the crevice opening was caused by the fact that a potential gradient existed between the anodic sites in the crevice and the cathodic sites outside of the crevice.  $\text{Cl}^-$  ions migrated to the corrosive occluded zone to maintain a charge balance because of superfluous cations from the following reactions in the anodic site of the crevice:



The accumulation of  $\text{Cl}^-$  ions at the anodic region may be one of the conditions required to sustain and promote the crevice corrosion propagation.<sup>21</sup>

### Pitting Corrosion

Figure 9 displays an image of  $\text{Cl}^-$  ion concentration around the 18/8 SS surface exposed to a 0.5-M/L  $\text{FeCl}_3$  solution. Results were obtained by a scanning combination  $\text{Cl}^-$  ion-selective liquid membrane microelectrode over the test surface. When pitting corrosion occurred, a nonuniform distribution of  $\text{Cl}^-$  ions near the metal/solution interface was observed. Further, results also showed that the higher the pitting corrosion activity, the higher the  $\text{Cl}^-$  ion concentration at the corroded area. When pitting corrosion ceased, the chloride contour maps showed little difference in the concentration of  $\text{Cl}^-$  ions around the metal/electrolyte interface. These results confirmed previous observations that the localized  $\text{Cl}^-$  ion concentration inside corroded pits plays a critical factor in maintaining pitting growth.<sup>22-23</sup> Local  $\text{Cl}^-$  ion concentration difference was not only necessary for the pitting initiation, but also one of the determining factors in stabilizing the propagation of pitting corrosion. The accumulation of  $\text{Cl}^-$  ions at pitted sites suppressed the repassivation of the pitting and promoted the development of pitting corrosion. Consequently, it may be possible to monitor the propagation process of pitting corrosion by in-situ imaging of the distribution of  $\text{Cl}^-$  ion concentration around the pitted area.

## CONCLUSIONS

- ❖ Information on the distribution of  $\text{Cl}^-$  ions near a metal/solution interface is essential for understanding localized corrosion of metals in electrolytes.
- ❖ Combination solid Ag-AgCl and combination liquid membrane  $\text{Cl}^-$  ion-selective microelectrodes were designed and constructed. These microelectrodes, which had micrometer-sized tips, contained two compartments, one that served as the reference electrode and the other as the  $\text{Cl}^-$  ion-selective electrode. The microelectrodes were used to measure in-situ  $\text{Cl}^-$  ion distribution around the corroded areas of several localized corrosion systems.
- ❖ Results demonstrated that the two microprobes, when used with a computerized scanning stage, can map the distribution of  $\text{Cl}^-$  ions near the metal/electrolyte interface. Under a simulated microgalvanic condition,  $\text{Cl}^-$  ions migrated toward and accumulated near the anodic areas. Such accumulation of  $\text{Cl}^-$  ions in the anodic region of crevice and pitting corrosion plays an important role in sustaining the propagation of localized corrosion.

## ACKNOWLEDGMENTS

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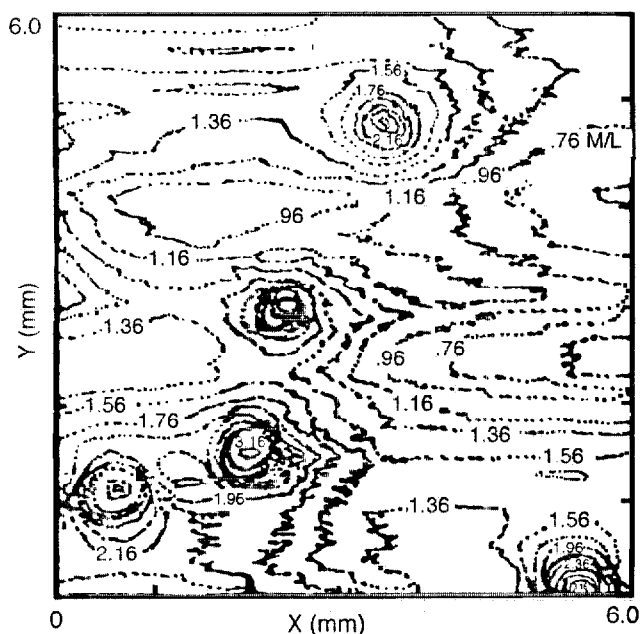


FIGURE 9.  $\text{Cl}^-$  concentration contour map obtained using solid  $\text{Cl}^-$  ion-selective microelectrode for a 18/8 SS surface in 0.5 M/L  $\text{FeCl}_3$  solution (pitting corrosion environment).